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(54) **Combustible compositions containing gas oil, methanol and a fatty acid ester, for use in particular for supplying diesel engines**

(57) A diesel fuel comprises from 20 to 90% by volume of at least one gas oil, from 5 to 60% by volume of methanol, and from 5 to 60% by volume of at least one C₁₋₃ alkyl ester

of a C₆₋₂₂ saturated or unsaturated fatty acid. The cetane number of the composition should be at least 40 and if necessary a cetane-number-improving additive may be added. The ester is preferably derived from a C₁₄₋₂₂ unsaturated acid or a C₆₋₁₄ saturated acid and may be obtained by transesterification of a fatty substance of vegetable or animal origin.

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SPECIFICATION

Combustible compositions containing gas oil, methanol and a fatty acid ester, for use in particular for supplying diesel engines

The present invention concerns novel combustible compositions that can be used in particular for
5 fuelling diesel engines.

It is known that methanol is not soluble under normal conditions in most gas oils, even those having the highest proportions of aromatic hydrocarbons, and it would be interesting if methanol could be substituted for a part of the gas oil in diesel engine fuels, as has been possible in petrols for controlled ignition engines.

10 However, if an attempt is made to replace gas oil by methanol, it is necessary to overcome the difficulties resulting from the reduction in the cetane number, which is markedly more substantial with methanol than with any other substance that it might be desired to introduce into gas oil, as well as the above-indicated problems involving solubility.

Certainly, there are agents that render methanol and gas oils compatible. In this connection, 15 reference may be made, for example to alcohols that are heavier than methanol, such as butanol, or butanol-acetone mixtures, but such substances must be added in substantial proportions: moreover, they have no favourable effect on the cetane number of the mixture and they usually do not enable a satisfactory level of viscosity to be attained.

The present invention results from the discovery that relatively substantial proportions of 20 methanol can be rendered compatible with gas oils, using an agent in the form of fatty acid esters as will be defined hereinafter. Using such fatty acid esters also makes it possible to maintain the cetane number of the mixtures at values that are acceptable for diesel fuels, and satisfactory levels of viscosity.

The combustible compositions of the present invention comprise from 20% to 90% by volume of at least one gas oil; from 5 to 60% by volume of methanol; and from 5 to 60% by volume of at least one 25 C_{1-3} alkyl ester of a C_{6-22} monocarboxylic acid with a saturated or unsaturated aliphatic hydrocarbon chain.

The gas oils involved in the present invention are conventional gas oils, that is to say, cuts of petroleum origin that boil in a range of from 120—190°C to 300—380°C, with a mean molecular weight of about 200 (the molecular weight of the constituents of the gas oils can range from about 130 30 to about 250). They also have a variable proportion of aromatic hydrocarbons (for example from 20 to 35% by weight). Their kinematic viscosity at 20°C is generally a few centistokes, for example from about 4 to 9 cSt. They have a cetane number of 38 to 58. Such gas oils may result from atmospheric distillation of crude oil or other refining operations such as cracking or hydrocracking.

Examples of fatty acid esters that can advantageously be used include methyl esters, ethyl esters 35 and isopropyl esters of saturated aliphatic acids such as caproic acid (C_6), enanthic acid (C_7), caprylic acid (C_8), pelargonic acid (C_9), capric acid (C_{10}), undecanoic acid, lauric acid (C_{12}), tridecanoic acid and myristic acid (C_{14}); and methyl esters, ethyl esters and isopropyl esters of aliphatic acids having one ethylenic unsaturation such as myristoleic acid (C_{14}), palmitoleic acid (C_{16}), oleic acid (C_{18}), gadoleic acid (C_{20}) and erucic acid (C_{22}). Methyl esters are preferred.

40 The saturated or unsaturated fatty acid esters considered in the present invention enjoy good solubility in gas oils, and a good degree of compatibility with the methanol, whose dissolution in the gas oils in substantial amounts they therefore facilitate. This faculty, which occurs at ambient temperature and above, is usually retained at temperatures lower than ambient.

The fatty acid esters used in the invention may be prepared from the fatty acids themselves when 45 they are readily available. In that case, operation is by means of simple esterification by means of the suitable C_1 to C_3 alcohol (for example, methanol, ethanol or isopropanol), using any conventional method.

They may also be prepared by transesterification from esters in which the alcohol residue is derived from other than C_{1-3} alcohols. This process is particularly applicable when the raw materials to 50 be used are natural fatty substances (e.g. oils or greases of vegetable or animal origin) comprising mixtures of glyceric esters of various saturated or unsaturated fatty acids. Examples of fatty substances of vegetable origin include colza, sunflower, soya, maize, cotton, almond, groundnut, olive, palm, palm-cabbage, coconut and copra oils.

55 Castor oil (in particular mamona oil) and linseed oil may also be mentioned. However, the last two have a degree of unsaturation that is much too substantial to produce alkyl esters that can be used as constituents of diesel fuels. In order to be able to use those oils, they will have to be stabilized by being subjected to preliminary partial hydrogenation.

Lard and tallow can be mentioned as examples of fatty substances of animal origin. 60 In order to produce the esters or the mixtures of esters required, transesterification is carried out by means of methanol (for example using the process disclosed in U.S. Patent No. 2 360 844), ethanol or isopropanol, according to circumstances.

When in accordance with the invention, combustible compositions containing for example from about 5 to 15% or in some cases up to 20% by volume of methanol are to be prepared, it is advantageous for the fatty acid ester used to comprise at least one methyl, ethyl or isopropyl ester of a

fatty acid with a long unsaturated chain (or a mixture of methyl, ethyl or isopropyl esters of fatty acids containing a substantial proportion of fatty acids with a long unsaturated chain). Such fatty acids contain for example from 14 to 22 carbon atoms and they essentially comprise the above-mentioned acids, namely myristoleic, palmitoleic, oleic, linoleic, gadoleic and erucic acids, and also mixtures of fatty acids derived from colza, sunflower, soya, maize, cotton, almond, groundnut, olive, palm and palm-cabbage oils, lard and tallow. 5

Consideration will be more particularly given, in accordance with the invention, to colza oils in which the "acid" part contains a reduced proportion of erucic acid, soya oil, cotton oil and palm oil (in particular Dende palm oil); and to lard.

10 The following Table sets out the main fatty acids that form the "acid" part of such oils and greases. 10

| acid % by weight | oil | colza | soya | cotton | palm | lard |
|---------------------|-----|-------|------|--------|------|------|
| palmitic | — | 6.5 | 21 | 43 | 27 | |
| stearic | — | — | — | — | — | 19 |
| oleic | 65 | 33.5 | 43.5 | 44.5 | 42 | |
| linoleic | 20 | 52.5 | — | — | — | |
| linolenic | 8 | — | — | — | — | |

Under these circumstances, the particular compositions considered contain from 20 to 90% by volume of gas oil; from 5 to 20% by volume of methanol, and from 5 to 60% by volume of fatty acid ester. 15

Such compositions have particularly high cetane numbers of about 40 or higher.

If it is desired to form combustible compositions containing more substantial proportions of methanol, for example up to 50% by volume, methyl, ethyl or isopropyl esters of fatty acids with a relatively shorter saturated chain may advantageously be used. These involve more particularly fatty acids containing from 6 to 14 carbon atoms, for example caproic, caprylic, capric and lauric acid, or myristic acid, or mixtures of acids originating from natural fatty substances such as copra oil and coconut oil. 20

Consideration will be more particularly given, in accordance with the invention, to coconut oil (in particular "babassu" oil), the "acid" part of which primarily contains about 48% of lauric acid, about 17.5% of myristic acid and about 9% of palmitic acid. 25

The particular combustible compositions which are considered in this case contain from 25 to 70% by volume of gas oil; from 10 to 50% by volume of methanol, and from 20 to 60% by volume of fatty acid ester.

The combustible compositions according to the invention that contain the largest amount of methanol (for example more than 30%) may have a cetane number that is too low for satisfactory use as base fuels for diesel engines. In this case, it is possible to increase the cetane number by resorting to conventional additives such as alkyl nitrates (for example amyl, hexyl or octyl nitrate), which are then added in proportions of from 0.1 to 6% by weight, so as to produce a suitable cetane number, for example 40 or higher. 30

35 An additional advantage of using fatty acid esters in order to render methanol compatible with gas oils is that, as those fatty acid esters make it possible to maintain a sufficiently high level of viscosity, they therefore make it possible to combat wear in the injection systems of diesel engines (pumps), such wear generally being found when gas oils containing alcohols to supply such engines are used.

40 Moreover, when used as fuels for diesel engines, it is possible for the compositions according to the invention to have added to them various conventional additives that are compatible with the fatty acid esters used. Thus, anti-oxidants may be incorporated as well as other additives, e.g. for improving the cold characteristics and anti-smoke additives.

45 The following examples illustrate but do not limit the invention. Examples 1, 14 and 15 are given by way of comparison.

In these examples, use is essentially made of two different gas oils, referred to as gas oil 1 and gas oil 2, the main characteristics of which are set out hereinafter:

| | | | |
|-----------|--------------------------------|---------------|----|
| Gas oil 1 | Specific gravity at 20°C | : 0.828 | |
| | Viscosity at 20°C | : 4.16 cSt | |
| | Cloud point | : -2°C | |
| | Pour point | : -18°C | |
| 5 | Filtrability limit temperature | : -8°C | 5 |
| | Distillation range | : 167—359°C | |
| | Aromatics content | : 24% | |
| | Cetane number | : 54 | |
| Gas oil 2 | Specific gravity at 20°C | : 0.848 | |
| 10 | viscosity at 20°C | : 3.66 cSt | 10 |
| | Cloud point | : -23°C | |
| | Pour point | : -27°C | |
| | Filtrability limit temperature | : -23°C | |
| | Distillation range | : 182 — 329°C | |
| 15 | Aromatics content | : 35% | 15 |
| | Cetane number | : 42.4 | |

In addition, inter alia fatty acid esters, methyl esters of various vegetable oils and methyl esters of lard were also used. Preparation of methyl esters of vegetable oils is illustrated hereinafter by the preparation of methyl ester of colza oil.

20 Using a 10 litre glass Grignard reaction vessel provided with an agitator, a thermometer, a bottoms valve and an external heating means, there is introduced 5 kg of refined colza oil which has been previously dehydrated for a period of 2 hours at 100°C, under a pressure of from 6.5 to 7 millibars.

The colza oil, after treatment in this way, has an acid value of 0.05 mg KOH/g and a saponification index of 192 mg KOH/g.

25 The agitator is set in operation and the oil is heated to 55 to 60°C; thereafter, a solution comprising 876 g of absolute methanol and 9 g of metal sodium is incorporated therein over a period of 5 minutes. The mixture is left to react for 1 hour and then agitation is stopped.

30 After settling for 30 minutes, the lower phase which essentially comprises glycerine (650 g) is removed by way of the bottoms valve. 620 cm³ of distilled water which has been previously heated to a temperature of 60°C is then added to organic phase in the reaction vessel. After vigorous agitation for a period of 15 minutes, the mixture is left at rest for the same period. The aqueous washing phase which settles is removed as described above. The washing operation is repeated twice with 320 cm³ of water.

35 The organic phase recovered is dried on anhydrous sodium sulphate and then briefly filtered, followed by evaporation at 100°C under reduced pressure (6.5 to 7 millibars) for 1 hour, in order to remove therefrom the last traces of methanol.

40 4750 g of the desired product is finally obtained, and analysis of the product shows that the methyl ester content is higher than 95% by weight. The main characteristics of the mixture of esters are set out in Table 1 below.

40 Preparation of methyl esters of lard is also described hereinafter. Under operation conditions identical to those described above, alcoholysis is effected in respect of 6 kg of lard of commercial origin, which has been previously dehydrated at a temperature of 100°C under a pressure of 6.5 to 7 millibars, for a period of 2 hours. After treatment in this way, the lard has:

an acid value of 1.3 mg KOH/g, and

45 a saponification index of 199 mg KOH/g.

Alcoholysis is performed with 1090 g of absolute methanol and 14 g of sodium.

Analysis of the organic phase produced (6241 g) shows a methyl ester content of about 97% by weight. The main characteristics of this mixture of esters are set out in Table 1 below.

Table 2 below also shows certain characteristics of a methyl oleate, methyl laurate and isopropyl myristate, which are also used in certain examples.

TABLE I

| Product Characteristics | Methyl esters of colza oil | Methyl esters of lard |
|-------------------------------------|-------------------------------|--------------------------|
| Specific gravity (20°C) | 0.880 | 0.870 |
| Flash point (closed vessel) (°C) | 188 | 180 |
| Acid value (mg KOH /g) | 0.05 | 0.01 |
| Viscosity (cSt) at 50°C | 3.75 | 4.05 |
| Cetane number | 45 | 56 |
| Distillation | | |
| Starting point (°C) | 321 | 309 |
| Final point (°C) | 350 | 340 |

TABLE 2

| Product Characteristics | Methyl oleate | Methyl laurate | Isopropyl myristate |
|-------------------------------------|------------------|-------------------|------------------------|
| Specific gravity (20°C) | 0.875 | 0.870 | 0.853 |
| Saponification index (mg KOH /g) | 195 | 260 | 208 |
| Acid value (mg KOH /g) | 0.05 | 0.03 | 0.04 |
| Cetane number | 52.0 | 59.6* | 66.7** |

* Number of a 50% mixture in gas oil 1.

** Number of a 50% mixture in gas oil 2.

5 EXAMPLE 1 (comparative)

Methanol was mixed with each of gas oils 1 and 2 described hereinbefore, in respective proportions of 10 and 15% by volume of methanol for 90 and 85% by volume of each of the gas oils in question.

Complete separation of the constituents of the mixture is observed, that is to say, it is impossible to produce a homogenous mixture, even at elevated temperature.

EXAMPLE 2

The attempt is made to compatibilise increasing proportions of methanol with gas oils 1 and 2 as defined hereinbefore, using a methyl oleate as the third constituent. 5

It was possible to form compositions, the proportions (by volume) of which are set out below. The certain number of the resulting compositions is specified:

| | Gas oil 1 (%) | Methanol (%) | Oleate 1 (%) | Cetane number | |
|----|---------------|--------------|--------------|---------------|----|
| 10 | 76 | 5 | 19 | 52.8 | |
| | 57 | 5 | 38 | 47.0 | 10 |
| | 72 | 10 | 18 | 47.7 | |
| | 54 | 10 | 36 | 42.8 | |
| | 45 | 10 | 45 | 43.9 | |
| | 30 | 15 | 55 | 41.5 | |
| 15 | 20 | 20 | 60 | 39.9 | 15 |
| | Gas oil 2 (%) | Methanol (%) | Oleate 1 (%) | Cetane number | |
| | 45 | 10 | 45 | 42.3 | |
| | 42.5 | 15 | 42.5 | 39.3 | |

EXAMPLE 3

20 Compositions in accordance with the invention are formed by using a methyl oleate of a different origin. 20

The proportions by volume of the constituents and the cetane number of the mixtures produced are set out below:

| | Gas oil 1 (%) | Methanol (%) | Oleate 2 (%) | Cetane number | |
|----|---------------|--------------|--------------|---------------|----|
| 25 | 20 | 20 | 60 | 44.0 | 25 |
| | Gas oil 2 (%) | Methanol (%) | Oleate 2 (%) | Cetane number | |
| | 42.5 | 15 | 42.5 | 40.6 | |
| | | | | | |

EXAMPLE 4

Compositions in accordance with the invention were produced using the mixture of methyl esters 30 of colza oil, as described above. 30

| | Gas oil 2 (%) | Methanol (%) | Colza oil esters (%) | Cetane number |
|--|---------------|--------------|----------------------|---------------|
| | 50 | 15 | 35 | 41.2 |
| | 35 | 20 | 45 | 40.0 |

EXAMPLES 5 to 7

35 This Example involves the preparation of various mixtures of methyl esters of other vegetable oils, 35 gas oil and methanol. The proportions of the compositions produced and their cetane number are set out below.

| Gas oil % vol. | Methanol % vol. | Methyl esters of the following oils % vol. | Cetane number |
|-------------------|--------------------|--|------------------|
| (1) 50 | 15 | soya 35 | 39.8 |
| (1) 50 | 15 | cotton 35 | 41.5 |
| (2) 42.5 | 15 | palm 42.5 (Dende) | 40.2 |

EXAMPLE 8

Compositions in accordance with the invention were produced using the above-described mixture of methyl esters of lard:

5

| Gas oil 2 (%) | Methanol (%) | Lard esters (%) | Cetane number |
|---------------|--------------|--------------------|------------------|
| 43.5 | 13 | 43.5 | 41.0 |

5

EXAMPLE 9

The attempt was made to compatibilise increasing proportions of methanol with gas oil 1, as 10 defined hereinbefore, using methyl caproate.

The compositions formed are as follows:

| Gas oil (%) | Methanol (%) | Methyl caproate (%) | Cetane number |
|-------------|--------------|------------------------|------------------|
| 62.5 | 16.5 | 21 | 36.2 |
| 49.5 | 26 | 24.5 | 27.0 |
| 26.5 | 47 | 26.5 | 20 |

In order to improve the cetane number of each of the foregoing compositions, amyl nitrate was added thereto, in the respective proportions as follows: @.5%, 2% and 6% by weight, and compositions were produced, with the respective cetane numbers as follows: 42.4; 40.3; and 39.6.

20 EXAMPLE 10

The attempt was made in the same way to compatibilise increasing proportions of methanol with gas oil 1, using methyl caprylate as the third constituent.

The following compositions were formed:

| Gas oil (%) | Methanol (%) | Methyl caprylate (%) | Cetane number |
|-------------|--------------|-------------------------|------------------|
| 65.5 | 13 | 21.5 | 38.5 |
| 51.5 | 23 | 25.5 | 31.7 |
| 25 | 50 | 25 | 22.8 |

20

In order to improve the cetane number of each of these compositions, amyl nitrate was added 30 thereto, in the respective proportions as follows: 0.1%, 1% and 4% by weight, and compositions were produced, with the respective cetane numbers as follows: 41.0, 40.8 and 40.2.

30

EXAMPLE 11

Various compositions in accordance with the invention were produced, by using methyl laurate as the fatty acid ester (the proportions are specified by volume).

| | Gas oil 1 (%) | Methanol (%) | Methyl laurate (%) | Cetane number | |
|---|---------------|--------------|--------------------|---------------|---|
| | 42.5 | 15 | 42.5 | 40.2 | |
| | 40 | 20 | 40 | 36.8 | |
| 5 | 25 | 20 | 55 | 40.9 | 5 |

It was possible to improve the cetane number of the second composition (it was increased to 40.9) by the addition of 0.2% by weight of amyl nitrate.

EXAMPLE 12

The fatty acid ester used was isopropyl myristate. The following compositions were produced 10 (proportions by volume):

| | Gas oil 1 (%) | Methanol (%) | Isopropyl myristate (%) | Cetane number | |
|----|---------------|--------------|-------------------------|---------------|----|
| | 25 | 20 | 55 | 40.3 | |
| 15 | Gas oil 2 (%) | Methanol (%) | Isopropyl myristate (%) | Cetane number | 15 |
| | 42.5 | 15 | 42.5 | 40.7 | |

EXAMPLE 13

A composition in accordance with the invention was prepared, using methyl esters of coconut oil (babassu) as the fatty acid esters, and the cetane number thereof was determined:

| | Gas oil 1 (%) | Methanol (%) | Methyl esters (%) of coconut oil | Cetane number | |
|----|---------------|--------------|----------------------------------|---------------|----|
| 20 | 25 | 20 | 55 | 40.8 | 20 |

EXAMPLES 14 and 15 (comparative)

The following were used, to try to dissolve methanol in a gas oil:

25 — isobutyl oleate (Example 14) and
— 2-ethylhexyl oleate (Example 15).

Mixtures were prepared, containing 42.5% by volume of gas oil 2, 15% by volume of methanol and 42.5% by volume of each of the two esters referred to above.

The mixtures suffer from complete separation of the constituents thereof, even at elevated 30 temperature.

Tests on a Diesel Engine

Some of the compositions of the invention were tested in an agricultural tractor diesel engine (a speed of 2400 rpm), for 50 hours for each composition.

The compositions were the following mixtures (by volume):

35 1 gas oil 1: 54% — methyl oleate : 36% — methanol : 10%.

2 gas oil 2: 42.5% — isopropyl myristate : 42.5% — methanol : 15%.

3 gas oil 1: 25% — methyl laurate: 55% — methanol : 20%.

4 gas oil 1: 25% — methyl esters of "babassu" coconut oil : 55% — methanol : 20%.

These tests did not show any operating problem difficulty. No deposits at the injectors were 40 found. Moreover, it was found that the power output of the engine was maintained normally.

CLAIMS

1. A combustible composition comprising from 20 to 90% by volume of at least one gas oil, from 5 to 60% by volume of methanol, and from 5 to 60% by volume of at least one C_{1-3} alkyl ester of a C_{6-22} saturated or unsaturated fatty acid.

2. A composition according to Claim 1 comprising from 20 to 90% by volume of at least one gas oil, from 5 to 20% by volume of methanol, and from 5 to 60% by volume of at least one C_{1-3} alkyl ester of at least one unsaturated C_{14-22} fatty acid.

3. A composition according to Claim 2 in which the proportions of the constituents are such that 5 the cetane number is at least 40.

4. A composition according to Claims 2 or 3 in which the unsaturated fatty acid ester is methyl, ethyl or isopropyl oleate.

5. A composition according to Claim 2 or 3 in which the unsaturated fatty acid ester is the product of transesterification by methanol, ethanol or isopropanol of a fatty substance of vegetable or animal 10 origin, the acid part of which contains a substantial proportion of a C_{14-22} unsaturated fatty acid.

6. A composition according to Claim 5 in which the fatty substance of vegetable or animal origin is colza, sunflower, soya, maize, cotton, almond, groundnut, olive, palm or palm-cabbage oils, lard or tallow.

7. A composition according to any one of Claims 2 to 6 in which the fatty acid ester is a methyl 15 ester.

8. A composition according to Claim 1 comprising from 25 to 70% by volume of at least one gas oil, from 10 to 50% by volume of methanol, and from 20 to 60% by volume of at least one C_{1-3} alkyl ester of at least one C_{6-4} saturated fatty acid.

9. A composition according to Claim 8 in which the proportions of the constituents are such that 20 the cetane number is at least 40.

10. A composition according to Claim 8, that also contains a portion of cetane-number-improving additive sufficient to produce a value of at least 40.

11. A composition according to any one of Claims 8 to 10 in which the saturated fatty acid ester is methyl, ethyl or isopropyl caprylate, caproate, caprate, laurate or myristate.

12. A composition according to any one of Claims 8 to 10 in which the saturated fatty acid ester is 25 the product of transesterification by methanol, ethanol or isopropanol of a natural fatty substance, the acid part of which contains a substantial proportion of C_{6-14} saturated fatty acid.

13. A composition according to Claim 12 in which the natural fatty substance comprises coconut oil or copra oil.

14. A composition according to any one of Claims 8 to 13 in which the fatty acid ester is methyl 30 ester.

15. A composition according to any one of Claims 1 to 14 in which the gas oil comprises a cut of petroleum origin, the distillation range of which is from 120°C—190°C to 300°C—380°C, that has a cetane number of from 38 to 58.

16. A composition according to any one of Claims 1 to 15 that further contains a suitable 35 proportion of at least one anti-oxidant.

17. A composition according to Claim 1 substantially as hereinbefore described in any one of Examples 2 to 13.

18. A composition according to any one of Claims 1 to 17 as fuel in a diesel engine.